

## TREATMENTS TO ACCELERATE THE AIR-DRYING OF WASHED SHEARLINGS

S. J. VIOLA, M. L. FEIN, F. P. LUVISI, AND J. NAGHSKI

*Eastern Regional Research Laboratory\*  
Philadelphia, Pennsylvania 19118*

### ABSTRACT

Experimental work described in this report indicates that washable shearlings (chrome-glutaraldehyde combination tanned) can be air-dried in reasonable time without the use of heat or mechanical tumbling. This good drying rate can be achieved by treating the shearling with a water-repellent of the chrome-complex type. The effects of the treatment are evident through at least four wash-dry cycles. The use of an amphoteric fatty amino acid as a final rinse "softening agent," during the wash cycle, accelerates the drying even more, while it keeps the wool face from clumping and the leather part of the shearlings soft and pliable.



### INTRODUCTION

This Laboratory has published a series of papers concerned with the developments of washable leather and washable shearling bed pads (1-8). Tanning with a combination of glutaraldehyde and chrome produces a shearling that is resistant to the effects of washing in tepid to moderately hot, soapy water. This resistance lasts through many wash-dry cycles. For example, shearling pads tanned in this manner were tested extensively in hospitals, nursing homes, and with out-patients over a three-year period. The pads were found to be serviceable for as long as 28 months with as many as 54 launderings. This is a significant improvement over shearling pads produced conventionally that lasted only about six months or ten launderings (9). The improved pads are now on the market (10).

Experience has shown that during machine-drying of the washed shearlings, in hospital laundry equipment or in home dryers, the wool facing of shearlings will soon develop small bundles of wool fibers that, in subsequent wash-dry cycles, can form harsh, dry, tight clumps. A certain amount of clumping may not negate the effectiveness of a medical bed pad in preventing the development of bed sores. However, the relatively poor appearance due to even moderate clumping would not be acceptable in washable shearlings intended for throw rugs or wall decora-

\*Eastern Marketing and Nutrition Research Division, Agricultural Research Service,  
U. S. Department of Agriculture.

tion. These clumps can be eliminated in part if the washed shearling is simply hung up to dry instead of tumble-dried. In addition, the clumps can be prevented almost entirely by the use of the proper softening agent in the final rinse water, before the shearling is hung up to dry (8).

Wet leather normally dries rather slowly. Treatment of the leather to hasten drying under ambient air conditions would be of practical value and enhance the utility of the shearlings. This report is concerned with the evaluation of various treatments to speed the drying of laundered shearlings when hung up in ambient room or out-of-door air.

## EXPERIMENTAL

### Stock

All experiments were run on shearlings commercially tanned with a combination of chrome-glutaraldehyde and obtained in the crust stage (before staking). The shearlings were cut into pieces measuring 6 x 8 inches, and treated as described below:

### Pretreatment

Six crust shearling pieces were wet back in an agitator washer with tap water at a pH of 6.4. The pieces were then transferred to a small laboratory drum for one-half hour for acidification in a one percent solution of formic acid. The pieces were then washed free of excess acid in running water and passed through a hand wringer. Two pieces of these pretreated shearlings were used in each of treatments D, E, and F.

### Treatments

A. Duplicate untreated pieces were set aside as controls.

B. *T-4-1042 Resin\** (Dow Corning Corporation) *silicone resin* (11). Two crust shearlings were wet back in tap water and then drummed with a ten percent T-4-1042 Resin solution, one to one float, at 38°C. for 40 minutes. The pieces were then washed in water for five minutes.

C. *UCAR C-33 Silicone\** (Union Carbide Corporation) *silicone resin* (12). A five percent solution was applied to the dry shearling pieces with a paint brush. The leather portion of the shearling was saturated. The samples were "air-cured" for several days.

D. *Leather chemical FC-146\** (Scotchgard trademark, 3M Company) *chrome complex of a long chain fluorochemical* (13). Two of the shearling pieces described in Pretreatment above were drummed with a ten percent solution of 3M leather Chemical FC-146 in a one to one float at 38°C. for 40 minutes. The pieces were washed in water for five minutes.

\*Reference to a commercial product does not constitute recommendation by the U. S. Department of Agriculture over any other similar product not mentioned.

E. *Quilon\** (*E. I. DuPont de Nemours, Inc.*) *stearato chromic chloride, Werner type chromium compound* (14). Two of the shearling pieces, treated as described in Pretreatment above, were drummed with ten percent solution of Quilon in a one to one float at 38°C. for 40 minutes. The pieces were then washed in water for five minutes.

F. *Pentel 52\** (*Pennwalt Corporation*) *chrome complex of the Werner type, based on fluorochemicals* (15). Two of the shearling pieces described above were drummed with a ten percent solution of Pentel in a one to one float at 38°C. for 40 minutes. The work was done in a small drum, and the shearling pieces absorbed the float very quickly. At the end of the treatment, the pieces were washed in running water for five minutes.

All of the shearling pieces from Treatments B to F were set out to cure and air-dry under ambient conditions to a nominal "constant" weight which was achieved within 44 hours.

### Washing and Drying Tests

The shearling pieces were washed in an automatic household washer using the "push-button" program for woolen items. The active washing solution was 13 gallons of water containing 25 grams of soap (*Ivory Fakes\**), at approximately 45°C. In selected cases, for purposes of comparison, a softening agent (*Deriphat 151C\**, 25 grams) was added to the final rinse water (8). In all cases, the washer pieces were dried at ambient room temperature and humidity. The pieces were weighed at specific intervals for data to determine the rate of drying.

### DISCUSSION AND RESULTS

The time it takes for a washed shearling to dry when it is hung up in ambient air is of interest, especially if this type of drying is essential to prevent excessive clumping of the wool face. Of course, the drying time for unmatted wool under these conditions is relatively short compared to that for the wet leather portion of the shearling. Shearlings were treated with commercially available leather modifying materials that could conceivably shorten the drying time. The tests described here were run to estimate and compare the drying time under ambient conditions for wet shearlings (spun dry) which had been subjected to "water-repellent" treatments. The materials used in these treatments have been suggested and supplied to the leather industry for some time as water-repellents or as combination leather-fiber-lubricants and water-repellents.

The test series was designed to determine if the treatments would be effective through more than one wash-dry cycle. When the data were collected and plotted for four consecutive wash-dry tests, it was found that the relative positions of the curves, representing the several treatments, did not change. Figure 1 shows the data obtained for the third wash-dry cycle, which was typical for the series. The relative positions of the curves in Figure 1 can be compared directly because

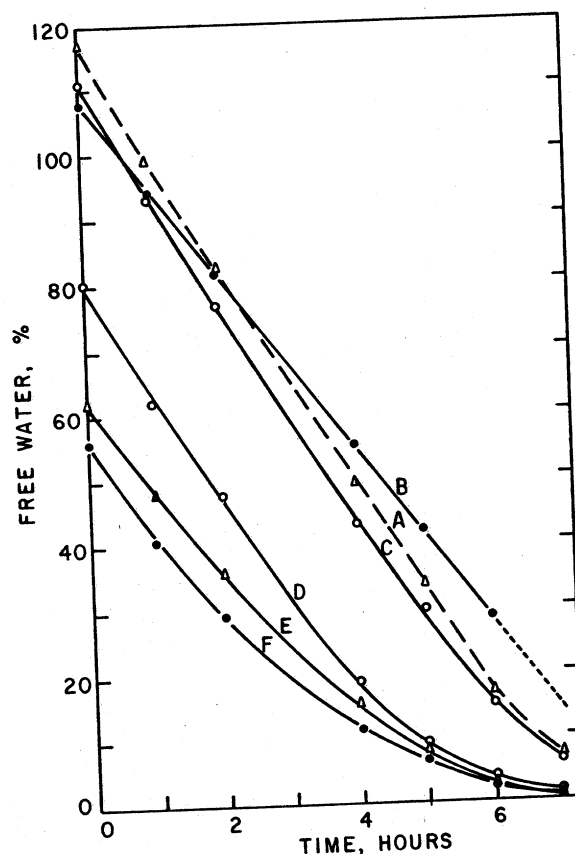


FIGURE 1.—The effect of the treatment of shearlings with water-repellent agents\* on the loss of free water ("Drying Rate") in ambient room air, during third wash-dry cycle.

\*A = untreated; B = Dow Corning T-4-1042 Resin; C = "UCAR;"  
E = "Quilon;" F = "Pentel;" D = "Scotchgard."

all the data used to plot them were obtained essentially at the same time. It is obvious that the chrome-complex materials were most effective. Under the test conditions used in this series of experiments, the silicone treatments were not effective as agents to help speed the drying of shearlings. The shearlings treated with silicones seemed to hold much more water after two spin cycles in the washing machine than those treated with chrome-complex agents. There was up to twice as much water to be evaporated from the skins.

Since the use of an amphoteric fatty amino acid (Deriphat 151C) as an after-rinse imparts such desirable qualities to washable shearlings (8), several experiments were run to show the effects of Deriphat 151C on the drying rate. Figure 2 shows drying curves for treated and untreated shearling pieces, with and without

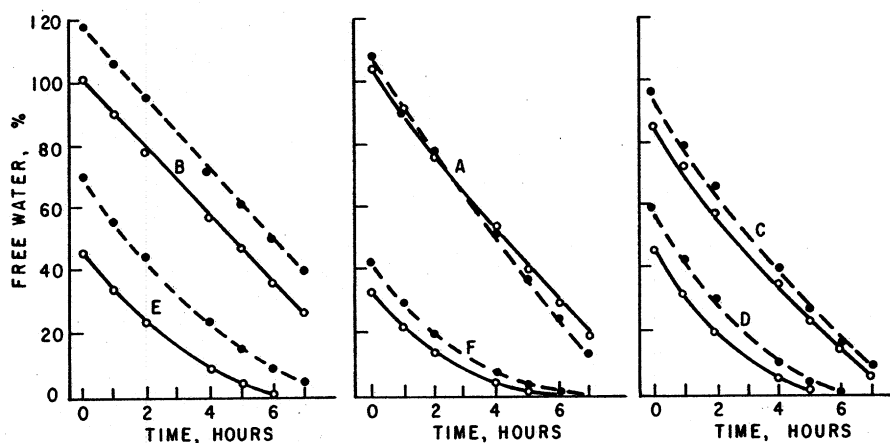


FIGURE 2.—The effect of the fatty amino acid "Deriphat 151C" as an after-rinse on the loss of free water ("Drying Rate") in ambient room air during the wash-dry cycle of shearlings treated with water-repellent agents.\* Dotted lines indicate data for washing with soap and water; solid lines indicate data for washing with soap and water, followed by rinse in "Deriphat 151C" solution.

\*A = untreated; B = Dow Corning T-4-1042 Resin; C = "UCAR;" E = "Quilon;" F = "Pentel;" D = "Scotchgard."

a Deriphat after-rinse. The data indicate that when the shearling has been treated with a water-repelling agent of the chrome-complex type, as described previously in this report, the Deriphat after-rinse will enhance the drying speed. These drying rates are directly comparable because the data used to plot the curves were obtained simultaneously during the same seven-hour period.

It is important to remember that the curves shown in Figures 1 and 2 are based on data obtained under "ambient conditions." It is believed that such conditions yielded data for this report that should approximate, very closely, the practical conditions found indoors in a large room. Since ambient conditions can be quite variable and possibly misleading, special effort was applied to see that the ambient conditions which were prevalent during the observations were the same for each sample subject to a given test. It is believed the relative rates of drying shown in Figures 1 and 2 will prevail under nominal changes in ambient conditions.

#### REFERENCES

1. Filachione, E. M., Fein, M. L., Harris, E. H., Luvisi, F. P., Korn, A. H., Windus, W., and Naghski, J. *JALCA*, 54, 668 (1959).
2. Fein, M. L., Filachione, E. M., Naghski, J., and Harris, E. H., Jr. *JALCA*, 58, 202 (1963).
3. Filachione, E. M., Fein, M. L., and Harris, E. H., Jr. *JALCA*, 59, 281 (1964).

4. Viola, S. J., and Fein, M. L. *The Leather Manufacturer*, 83, 16, 18, 20 (August, 1966).
5. Happich, W. F., Happich, M. L., Windus, W., Palm, W. E., and Naghski, J. *JALCA*, 59, 448 (1964).
6. Happich, W. F., Happich, M. L., Windus, W., and Naghski, J. *JALCA*, 64, 227 (1969).
7. Fein, M. L., Viola, S. J., and Filachione, E. M. U. S. Patent 3,300,338 (January 24, 1967).
8. Fein, M. L., Viola, S. J., and Naghski, J. *The Leather Manufacturer*, 86, 50 (November, 1969).
9. Happich, W. F., Windus, W., and Naghski, J. *Hospitals - Journal of the American Hospital Association*, 44, 112 (January 1, 1970).
10. Brownlowe, M. A., Cohen, F. R., and Happich, W. F. *American Journal of Nursing*, 70, 2368 (November, 1970).
11. Bulletin - Dow Corning T-4-1042 Resin. Aqueous Treatment for Leather. Dow Corning Corporation, Midland, Michigan 48641.
12. Bulletin F-41589 - Products for Leather, pp. 16 and 17. Union Carbide Corporation, 270 Park Ave., New York, N. Y. 10017.
13. Technical Data (sheets) - 3M Brand Leather Chemical FC 146. 3M Company, Chemical Division, St. Paul, Minnesota 55119.
14. Quilon Chrome Complex, Product Information Bulletin, Industrial and Biochemicals Department, Industrial Chemicals Division, E. I. DuPont de Nemours & Co., Inc., Wilmington, Del. 19898.
15. Data Sheet - Pentel 52, Fluorochemical Leather Treatment - Pennwalt Corporation, 3 Penn Center, Philadelphia, Pa. 19102.

# A NOTE ON THE SLUDGE FORMATION OF THE TAN LIQUORS IN THE TAN YARD\*

D. GHOSH, K.R.V. THAMPURAN, AND M. BALAKRISHNAN

*Central Leather Research Institute, Madras*

The Indian leather manufacturers use mainly aqueous extracts of babul and myrab for the manufacture of heavy leathers. Some tanners also use water extract of mangrove bark and wattle extract along with these two tanning materials. During tannage, plenty of sludge is accumulated in the tan pits, which are mainly from myrab liquors and partly from other liquors. It was reported<sup>1,2</sup> that the aqueous extracts of myrab and babul lose plenty of tanning in the form of sludge, when these are exposed to air. In the case of myrab, some of the components namely chebulinic acid and ellagic acid go out of the solution after a few days of extraction and settle at the bottom of the tan pit in the form of sludge. Moreover, part of gallic acid which is slightly soluble in water, is likely to be shifted out of the colloidal solution and settle with the previous two components. Highly polymerised tan molecules of condensed tanning materials likewise settle at the bottom of the pits in the form of sludge, after they exceed their critical limit.

The present experiment was undertaken to show the difference between the sludge formation in the tan pits containing blended liquors of hydrolysable and condensed tanning materials with and without pelt pieces.

## Experimental

h of crushed babul and mangrove barks were blended separately with 4 times of water and 4 times of crushed myrab nuts, and 4 times of water were given in each case, and were then kept for 18 hours and then filtered. One litre from each and in another litre, in each case, delimed pelt weighing

The blanks and the liquors with the pelts were then kept in each case for 15 days, after which the pelt pieces were taken out and washed. In all the cases the results were then determined after centrifuging the samples under vacuum. The results are given in the Table I.

Each of crushed babul and mangrove bark were blended with 4 times of water and 4 times of myrab in two beakers and 1600 ml. of water was added in each case. All these were kept in this condition for 18 hours and then filtered through cloth. Separately leached liquors of myrab, were then mixed with 4 times of water and 4 times of crushed babul and mangrove. The Barkometer strength and total solids were then noted. 4 pieces of delimed pelt were then put in the liquors maintaining the pelt/liquor ratio as 1 : 10. The pieces were then kept in the liquors for 15 days, after which the sludge formation was deter-

TABLE—I

## Sludge Formation in the Blended Liquors With and Without Pelts

<i>Experiment No.</i>	<i>Nature of blend (in quantity)</i>	<i>Volume of liquor</i>	<i>°BK</i>	<i>Sludge/litre (gm.)</i>
1.	Mangrove—3 + Myrab—1	1 litre	18	With pelt—7. Without pelt—6.7
2.	Babul—3 + Myrab—1	1 litre	18	With pelt—5.6 Without pelt—4.7

mined after centrifuging the liquors and drying the sludge in the vacuum pan to a constant wt. The results are given in the Table II.

TABLE—II

## Sludge Formation in the Used Liquors, (after tanning pelts).

<i>Experiment No.</i>	<i>Nature of blend (in quantity)</i>	<i>Volume of liquor collected</i>	<i>°BK</i>	<i>Wt. of sludge in gm.</i>	<i>Sludge/litre (gm.)</i>
1.	Mangrove—3 + Myrab—1	1050	18	7.25	6.9
2.	Babul—3 + Myrab—1	880	18	4.8	5.4
3.	Mangrove (3) and myrab (1) Separately leached and blended	1080	18	6.1	5.6
4.	Babul (3) and Myrab (1) Separately leached and blended	900	18	4.6	5.1



## Discussion of Results

From the results, it was observed that the sludge formation of both the blended liquors (babul+myrab and mangrove+myrab) used for tanning pelts, was slightly more than the liquors which were kept as blank : the blended liquors of mangrove and myrab showed more of sludge formation than those of babul and myrab.

Presumably, when the liquors were extracted from the blended tanning materials some components which are otherwise insoluble are extracted because of mutual solubilisation effect<sup>3</sup> and held in suspension by the solubilised tan molecules. But the equilibrium of the liquor is likely to get disturbed when the tan molecules responsible for keeping some of the components in suspension, penetrate through the pelts; with the result, the suspended components presumably precipitate in the form of sludge. This might explain more of sludge formation in the liquors where pelts are tanned. The experiment thus showed that the conception<sup>4</sup>, that the peptised molecules penetrate through the pelt along with their carriers and act as fixed tans, may be fallacious.

In the case of mangrove tannis, which are mainly based on leucocyanidin<sup>4,5</sup> and which contain comparatively higher particle size as compared to babul are likely to get polymerised quickly during tanning and a part of it precipitates in the form of sludge when these exceed their critical limit. Those precipitated molecules are likely to weigh more than those of babul molecules. This would presumably suggest more yield of sludge in the mangrove-myra liquor.

Sludge formation was found to be more in the used liquor (in which pelt was tanned) derived from the blended materials prior to leaching as compared to that made up with liquors, leached separately and then blended. The sludge formation in the case of babul and myrab blends, however, did not show much difference in both the cases. The penetration of both the liquors through the pelts was found to be almost the same.

The yield of sludge in both the cases of the blends of babul and myrab was found to be much less as compared to those of mangrove and myrab. One reasonable explanation might be that the volume collected in the case the blends of babul and myrab are much less than those of mangrove and myrab and consequently the difference in the sludge formation. Other probable reasons have already been explained before.

This experiment thus showed that if the hydrolysable and condensed tanning materials are first blended prior to leaching and then the leach liquor is used for tanning, the sludge formation in the tan pits is not minimised, rather it is increased in some cases. It was suggested that the different types of tanning material could only be blended the leached when the solubility and tan content of the materials are almost the same or differ only slightly. Otherwise, the one which is

more soluble in water is extracted first thereby decreasing considerably the solubility of the tannins of other tanning materials. In the case of the blend of mangrove and myrab the solubility of the former is much less than that of the latter<sup>7</sup> and consequently when these two types of tanning materials are blended and extracted, myrab being highly soluble in water is extracted first thus obstructing the mangrove extractives from coming into solution. This would result in more of myrab infusion in the blended extract, which being more of sludge forming materials, results in more sludge in the tan pits. On the other hand, the solubility of crushed babul was found to be slightly less than that of crushed myrab<sup>7</sup> and hence sludge formation in both these cases did not show much of difference; the blended the leached one giving slightly higher figure than the one leached separately and blended.

### References

1. Santhanam P.S., Barat S.K., *Leather Science* 10, 41 (1963)
2. Santhanam P.S., Ghosh D., and Nayudamma Y. *Leather Science*. 14, 179 (1967)
3. White T., and Kirby K.S., *J.S.L.T.C.* 36 148 (1952)
- 3-a. Gustavson K.H. *The Chemistry of Tanning Processes*, Academic Press, 1956 Page 197.
4. Cunningham, G.E. Eade, R., and Ghosh D., *Bulletin, CLRI*, 9.33 (1962)
5. Ghosh D.—unpublished result.
6. Pollak L., *J.A.L.C.A.* 29 174, (1934)
7. Ghosh D., Thampuran K.R.V., and Balakrishnan, M., *The Tanner*, 21, 209, (1967).

### Acknowledgement

The authors thank Dr. S. K. Barat for his encouragement and guidance in this work. Thanks are due to the authorities of the United States Department of Agriculture for the generous grant under PL-480 programme, which made this work possible. Thanks are also due to the Director, C.L.R.I. for permission to present this paper at this Symposium.

---

\* Paper presented at the ILTA Symposium 1969 at Batanagar.

4. Viola, S. J., and Fein, M. L. *The Leather Manufacturer*, 83, 16, 18, 20 (August, 1966).
5. Happich, W. F., Happich, M. L., Windus, W., Palm, W. E., and Naghski, J. *JALCA*, 59, 448 (1964).
6. Happich, W. F., Happich, M. L., Windus, W., and Naghski, J. *JALCA*, 64, 227 (1969).
7. Fein, M. L., Viola, S. J., and Filachione, E. M. U. S. Patent 3,300,338 (January 24, 1967).
8. Fein, M. L., Viola, S. J., and Naghski, J. *The Leather Manufacturer*, 86, 50 (November, 1969).
9. Happich, W. F., Windus, W., and Naghski, J. *Hospitals - Journal of the American Hospital Association*, 44, 112 (January 1, 1970).
10. Brownlowe, M. A., Cohen, F. R., and Happich, W. F. *American Journal of Nursing*, 70, 2368 (November, 1970).
11. Bulletin - Dow Corning T-4-1042 Resin. Aqueous Treatment for Leather. Dow Corning Corporation, Midland, Michigan 48641.
12. Bulletin F-41589 - Products for Leather, pp. 16 and 17. Union Carbide Corporation, 270 Park Ave., New York, N. Y. 10017.
13. Technical Data (sheets) - 3M Brand Leather Chemical FC 146. 3M Company, Chemical Division, St. Paul, Minnesota 55119.
14. Quilon Chrome Complex, Product Information Bulletin, Industrial and Biochemicals Department, Industrial Chemicals Division, E. I. DuPont de Nemours & Co., Inc., Wilmington, Del. 19898.
15. Data Sheet - Pentel 52, Fluorochemical Leather Treatment - Pennwalt Corporation, 3 Penn Center, Philadelphia, Pa. 19102.